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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B01D 53/34, F23G 7/06	A1	(11) International Publication Number: WO 93/0795 (43) International Publication Date: 29 April 1993 (29.04.93)
(21) International Application Number: PCT/SE92/00576 (22) International Filing Date: 24 August 1992 (24.08.92) (30) Priority data: 9103008-0 16 October 1991 (16.10.91) SE (71)(72) Applicant and Inventor: HEED, Björn [SE/SE]; Utlandagatan 19, S-412 61 Göteborg (SE). (74) Agent: AWAPATENT AB; Box 53252, S-400 16 Göteborg (SE). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CS, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, PL, RO, RU, SD, SE, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).		Published <i>With international search report. In English translation (filed in Swedish).</i>

(54) Title: A METHOD OF REMOVING NITROGEN OXIDES FROM A GAS FLOW BY USING A COMBUSTION EXCHANGER**(57) Abstract**

The invention concerns a method of removing nitrogen oxides from a gas flow by using a combustion exchanger. Reducing nitrogen compounds are mixed with the gas before the latter is treated in the combustion exchanger.

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A METHOD OF REMOVING NITROGEN OXIDES FROM A GAS FLOW BY
USING A COMBUSTION EXCHANGER

5 Most combustion systems incorporating combustion engines emit exhausts containing nitrogen oxides. Emission of nitrogen oxides into the atmosphere is a potential danger to the environment that has many aspects, such as excessive fertilization, acidification, direct poisonous
10 effects and secondary formation of poisonous substances, such as photo-chemical oxidants, for example.

 The exhausts from combustion systems mostly contain a certain oxygen surplus originating from the combustion stage and they are oxidants by nature, which makes it
15 difficult to reduce the nitrogen oxides by using ordinary reducing agents. However, one has found that it is quite possible to employ various method of what is known as selective reduction of the nitrogen oxides. As the reducing agent is used ammonia, carbamide or other
20 substances that contain nitrogen, such as amines. To simplify, the method could be said to involve reacting positive valence nitrogen in nitrogen oxides with negative valence nitrogen to form nitrogen of zero valence, i.e. harmless nitrogen gas molecules.

25 To allow such reactions to be utilized does, however, require either medium high temperatures (200-500°C) and the effects of a stationary catalyst in honeycomb or particle-bed form, a method known as selective catalytic reduction, SCR, or the effect may be achieved without
30 stationary catalysts but in this case considerably higher temperatures (500-900°C) are required. By analogy, the latter method usually is referred to as selective non-catalytic reduction, SNCR.

 Whichever method is adopted, it is necessary to pay
35 attention to and carefully control the amount of reducing agent that is added in order to avoid excessive effluents of such agents, too, which are not either quite harmless.

The reducing agents not spent in the reaction with nitrogen oxides will exit together with the gas stream as so called "slip". Sometimes, particularly in the case of SNCR, it is disadvantageous to have to work at comparatively high temperatures. Heating of large volumes of gas might be very expensive and entail considerable operation costs.

In accordance with the teaching of the subject invention a combustion exchanger (European Patent 218 590) may be used to reduce the nitrogen oxide contents in a gas flow. This eliminates the problem of slip in reducing agents while at the same time the heating costs are kept low.

The method could be described as follows: When the gas flow does not contain suitable reducing agents, such agents are added and are mixed into the gas flow. The latter is then passed through a combustion exchanger wherein the gas is heated successively up to a high temperature level, whereafter it is successively cooled to a temperature level close to the starting temperature. Since heat can be borrowed only temporarily by the gas and the main portion of the heat is immediately recovered by the combustion exchanger, the energy consumption of this heat treatment is low.

The gas is heated successively, and thus it will pass through the temperature range within which the reaction of nitrogen oxide reduction occurs. Thus, amounts of reducing agents are being spent during the desired reaction process, any excess amounts of reducing agent being left in the gas. However, the gas is thereafter heated further to a temperature ensuring reaction also of these excess amounts, which are destroyed through reaction with the oxygen contained in the gas.

To summarize, the treatment in the combustion exchanger comprises both reduction reactions and oxidation reactions, eliminating nitrogen oxides as well as unspent nitrogen oxide reducing agents. The oxidation step there-

fore could provide the added advantage of removing also other pollutants that can be oxidized, such as carbon monoxide, hydrocarbons, hydrogen gas, and so on.

In the case of gas mixtures, and particularly with respect to the components therein that can be oxidized, the selective reduction of nitrogen oxides that is primarily aimed for should, for optimum efficiency, be effected at different temperature levels, depending on the composition of the gas. The optimum temperature further depends on the reducing agent that is used. In this respect the use of a combustion exchanger has the advantage of exposing the gas mixtures to all relevant temperatures, and consequently the chances of reaction are very favourable. In other words, the composition of the gas need not be known beforehand, nor is it necessary to adapt the heating to different situations.

The nitrogen oxide reducing agents that are added to the gas flow could be in gaseous form, for instance ammonium from a pressurized vessel. This makes admixture into the gas flow prior to entrance into the combustion exchanger easy. Since the added amount normally is small in comparison with the volume of the gas, the addition could also be in the form a liquid which is vaporized as it is admixed with the gas flow. In this case, the liquid could either be in the form of an essentially pure substance or in the form of a liquid solution of the active ingredient.

The addition need not necessarily consist of one single active substance. Since the treatment in the combustion exchanger involves treatment at all relevant temperature levels, mixtures of a several different components having different optimum reaction temperatures, could be used without disadvantage. The addition could also contain a number of irrelevant components without disturbance. Those not used for the nitrogen oxide reduction process are destroyed at higher temperature levels. For this reason it may be economically

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advantageous as well as environmentally safe to use
urine and liquid manure for the nitrogen oxide reduction
in accordance with the method of the invention.

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CLAIMS

1. A method of removing nitrogen oxides from a gas flow by using a combustion exchanger, characterized by mixing one or several reducing nitrogen compounds with the gas before the latter is treated in the combustion exchanger.

2. A method as claimed in claim 1, characterized in that ammonium is used as the reducing nitrogen compound, said ammonium being sprayed into the gas flow in liquid or gas form.

3. A method as claimed in claim 1, characterized in that a liquid solution of ammonium is used as the reducing nitrogen compound, said liquid solution being sprayed into and vaporized in the gas flow.

4. A method as claimed in claim 1, characterized in that a liquid solution of carbamide is used as the reducing nitrogen compound, said liquid solution being sprayed into and vaporized in the gas flow.

5. A method as claimed in claim 1, characterized in that animal urine and animal liquid manure are used as the nitrogen oxide reducing agent.

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INTERNATIONAL SEARCH REPORT

International Application No **PCT/SE 92/00576**

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: B 01 D 53/34, F 23 G 7/06																	
II. FIELDS SEARCHED <div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched⁷</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 25%; padding: 5px;">Classification System</td> <td style="padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC5</td> <td style="padding: 5px;">B 01 D; F 23 G</td> </tr> </table> <p style="text-align: center; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</p> <p style="margin-top: 10px;">SE,DK,FI,NO classes as above</p>			Classification System	Classification Symbols	IPC5	B 01 D; F 23 G											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category *</th> <th style="width: 70%; padding: 5px;">Citation of Document,¹¹ with Indication, where appropriate, of the relevant passages¹²</th> <th style="width: 20%; padding: 5px;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">SE, B, 441623 (BJÖRN HEED) 21 October 1985, see the whole document --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-5</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">SE, B, 466433 (BJÖRN HEED) 17 February 1992, see the whole document --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-5</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">WO, A1, 8910182 (FUEL TECH, INC.) 2 November 1989, see the whole document --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-5</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">WO, A1, 9005578 (MCNEILL, KEITH, RUSSEL) 31 May 1990, see the whole document -- -----</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-5</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	SE, B, 441623 (BJÖRN HEED) 21 October 1985, see the whole document --	1-5	A	SE, B, 466433 (BJÖRN HEED) 17 February 1992, see the whole document --	1-5	A	WO, A1, 8910182 (FUEL TECH, INC.) 2 November 1989, see the whole document --	1-5	A	WO, A1, 9005578 (MCNEILL, KEITH, RUSSEL) 31 May 1990, see the whole document -- -----	1-5
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<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; padding: 5px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="padding: 5px;">14th January 1993</td> <td style="text-align: center; padding: 5px;">20 -01- 1993</td> </tr> <tr> <td style="padding: 5px;">International Searching Authority</td> <td style="padding: 5px;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center; padding: 5px;">SWEDISH PATENT OFFICE</td> <td style="text-align: center; padding: 5px;">BRITT-MARIE LUNDELL</td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	14th January 1993	20 -01- 1993	International Searching Authority	Signature of Authorized Officer	SWEDISH PATENT OFFICE	BRITT-MARIE LUNDELL							
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		DE-T- 3590307	87-06-04
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